Neutron Scattering Investigation of Magnetic Bilayer Correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$

R. Osborn[1], S. Rosenkranz[1], D.N. Argyriou[2], L. Vasiliu-Doloc[3*], J. W. Lynn[3*], S.K. Sinha[4], J.F. Mitchell[1], K.E. Gray[1], S.D. Bader[1]

[1]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*
[2]*Manual Lujan, Jr. Neutron Scattering Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[3]*NIST Center for Neutron Research, National Institute of Science and Technology, Gaithersburg, Maryland 20899*
[4]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439*

(February 1, 2008)

Neutron scattering investigations of the paramagnetic correlations in the layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$, which exhibits colossal magnetoresistance above the Curie transition at $T_C = 112$ K, show that spins in neighboring layers within each bilayer are strongly canted at an average angle that is dependent on both the magnetic field and temperature, as predicted by de Gennes. The in-plane correlation length does not diverge at T_C, although the magnetic Bragg intensity obeys critical scaling below T_C, with the same temperature dependence as the zero-field electrical conductance.

75.25.+z, 75.40.-s, 75.40.Cx, 72.15.-v

Naturally layered manganites have proved to be fruitful systems for understanding the mechanism of colossal magnetoresistance (CMR) and have become the focus of many recent investigations into this phenomenon [1–6]. The reduced dimensionality increases the magnitude of the CMR, although at the cost of reducing the ferromagnetic transition temperature to about 100 K [1]. However, the extended temperature range over which ferromagnetic correlations are significant and their strong anisotropy allow a detailed examination of the link between local spin correlations and the resulting magnetotransport. The extra freedom afforded the crystal chemist by the layered structure may also lead to better-optimized materials for industrial applications.

The majority of experiments have been performed on the Ruddlesdon-Popper phases with the general formula $(La_{1-x}Sr_xMnO_3)_nSrO$, which comprise n layers of corner-shared MnO_6 octahedra separated by $(La,Sr)O$ blocking layers. In particular, the two-layer compounds have revealed a rich variety of properties which are strongly dependent on x [2]. Although most investigations of three-dimensional CMR compounds have concentrated on the possible role of electron-lattice interactions [7–9], of equal importance in the two-dimensional compounds has been the influence of antiferromagnetic interactions competing with the ferromagnetic double-exchange. Perring *et al* [3] have reported evidence of weak antiferromagnetic correlations within the planes above T_C that are fluctuating rapidly and are believed to coexist with the ferromagnetic correlations. On the other hand, Argyriou *et al* [5] have inferred the existence of a canting of the ordered moments below T_C from

the change in sign of Mn-O bond compressibilities at the transition. This aspect of the problem is only now receiving the theoretical attention it deserves, even though de Gennes first considered it nearly forty years ago [10–12].

The work reported here is part of a general study linking the magnetic and transport properties of naturally layered manganites directly to the underlying magnetic correlations measured by neutron diffraction and spectroscopy. We find evidence that, although the magnetic correlations are predominantly ferromagnetic within the two-dimensional planes, there is much weaker ferromagnetic correlation between spins in neighboring layers within each bilayer. This observation is consistent with a canting of the spins in neighboring layers with a cant angle that is dependent on both magnetic field and temperature, becoming smaller as the temperature approaches T_C. The correlation is not confined to short-lived clusters, as were the antiferromagnetic fluctuations observed by Perring *et al* [3], but involves the critical fluctuations that lead to ferromagnetic ordering. Our results imply that there is a delicate balance between competing double exchange and superexchange interactions in these compounds. In the critical regime below T_C, the link between magnetic ordering and electrical transport is strikingly evident, with both displaying similar two-dimensional exponents.

An x = 0.4 single crystal, which we will refer to as the 40%-doped compound, $La_{1.2}Sr_{1.8}Mn_2O_7$, weighing 150 mg was grown in a double-mirror, floating zone image furnace. Bulk measurements show that the sample has a Curie transition at about $T_C = 112$ K, which also corresponds to the change from insulating to metallic transport both parallel and perpendicular to the MnO_2 planes. The lattice parameters are $a = 3.862$ Å and $c = 20.032$ Å at 125 K in good agreement with earlier measurements for this composition [4]. We saw evidence of a small crystallite in the sample with slightly smaler values of a and c and a T_C value of 114 K, which could therefore have slightly different dopant level. The only time that this presented a significant problem was when measuring the order parameter. However, improved collimation ensured that we were only measuring scattering from one crystallite. Diffuse neutron scattering studies were performed on the Single Crystal Diffractometer (SCD) at Los Alamos where a broad region of reciprocal space could be mea-

sured in one scan using a pulsed white beam. These were followed up by measurements using the triple-axis spectrometers BT2 and BT9 at Gaithersburg. For the measurements at BT9, we employed a superconducting solenoid to provide fields to 7 T applied in the ab plane. Using incident wavevectors of $k_i = 2.57$ and 2.662 $\mathring{A}^{-1}$ without energy analysis, we performed scans in the $[0k0]$ scattering plane $i.e.$ with the $[h00]$ and $[00l]$ reciprocal lattice vectors as orthogonal axes within the plane. The conductance was measured using a six-probe technique suitable for materials with highly anisotropic conductivities, such as the cuprate superconductors [13].

The SCD measurements, illustrated in Fig. 1, show that the scattering above T_C consists of rods parallel to the c-axis, $i.e.$ parallel to $[00l]$, at all integer h including $h = 0$. The rods are strongly temperature-dependent, becoming narrower as $T \to T_C$, consistent with magnetic scattering from predominantly ferromagnetic correlations which have much longer correlation lengths within the MnO_2 planes than perpendicular to them. Below T_C, the scattering results from inelastic spin wave excitations and so becomes much weaker with decreasing temperature. We also observe a weaker second component, peaked at $l = 0$, with a longer in-plane correlation length. Since this is nearly temperature-independent near T_C and has both magnetic and nuclear components, we believe that it arises from a low density of multilayer intergrowths, as identified by Potter et al [14], and have excluded it from our analysis.

In the triple-axis experiments, scans were performed both parallel and perpendicular to the rods $(00l)$ and $(10l)$. The magnetic neutron scattering cross section is proportional to

$$S(\mathbf{Q}) = \sum_{\alpha\beta} S^{\alpha\beta}(\mathbf{Q})$$
$$= \sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta\right) \langle S_\alpha(\mathbf{Q}) S_\beta(-\mathbf{Q}) \rangle \qquad (1)$$

$$\text{with } S_\alpha(\mathbf{Q}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} S_{\alpha,i} exp(i\mathbf{Q} \cdot \mathbf{r}_i),$$

where $\mathbf{Q}$ is the wavevector transfer, and $S_{\alpha,i}$ and $\mathbf{r}_i$ are the magnetic moments and atomic coordinates, respectively, of the Mn ions (α, β = x,y,z; the z-direction is parallel to the crystal c-axis). Because of the orientation factor in the paranthesis of Eq. 1, scans are only sensitive to magnetic fluctuations perpendicular to $\mathbf{Q}$. Therefore, scans along $\mathbf{Q} = [00l]$ will only measure in-plane correlations, $S^{xx}(\mathbf{Q}) + S^{yy}(\mathbf{Q})$, while scans along $[h0l]$ will be dominated by $S^{yy}(\mathbf{Q}) + S^{zz}(\mathbf{Q})$, for small values of l. By combining the results of scans along $[0.05\ 0\ l]$ and $[0.95\ 0\ l]$, we have been able to separate $S^{xx,yy}(\mathbf{Q})$ from $S^{zz}(\mathbf{Q})$.

If the only significant correlations are between Mn spins within a bilayer, $i.e.$ at $\mathbf{r}_i = \pm z\mathbf{c}$, then the rod scattering will be modulated as a function of l such that

$$S(\mathbf{Q}) = S^2[\frac{1}{2}\left(1 + \hat{Q}_z^2\right)\langle cos^2\gamma\rangle(1 + R\langle cos\theta\rangle cos4\pi zl)$$
$$+ \left(1 - \hat{Q}_z^2\right)\langle sin^2\gamma\rangle], \qquad (2)$$

where θ is the in-plane angle between spins in neighboring layers within the bilayer, γ is the angle of the spin with respect to the planes, and R = $\langle cos\gamma\rangle^2/\langle cos^2\gamma\rangle$ assuming that the z-axis spin components are uncorrelated $(8/\pi^2 \leq R \leq 1)$. Since S($\mathbf{Q}$) is determined by instantaneous (t = 0) spin correlations, the angular brackets represent ensemble averages over the crystal. In the 40% compound, z is 0.0964 so that a ferromagnetic modulation would peak at $l = 0$ and fall to zero at $l = 2.59$.

Short-range spin correlations within the plane produce a Lorentzian broadening of the rods with the half-width equal to the inverse correlation length. This is seen in Fig. 2(a), which shows a scan perpendicular to the $[10l]$ rod at $l = 1.833$, from which we can estimate the ferromagnetic in-plane correlation length to be 9.7 $\mathring{A}$ at 125 K. Scans at other values of l show that the correlation length is constant along the rod as expected.

The most striking observation is that the modulation along the rod, shown in Fig. 2(b) is very weak even close to T_C, indicating that $\langle cos\theta\rangle \ll 1$. From fits to Eq. 2, we have determined that $\langle cos\theta\rangle \simeq 0.06$ at 125 K in zero field, whereas, if the ferromagnetic correlations between the spins at $\pm z\mathbf{c}$ were as strong as those within the plane, then $\langle cos\theta\rangle$ would be approximately 0.67. Since we only measure the average value of $cos\theta$, and not its distribution, there are two reasonable interpretations of this observation.

The first is that the average value of θ is zero but that the correlations between the neighboring planes are much weaker than within the plane. In the double exchange mechanism, the mobile electrons lower their kinetic energy by polarizing the localized Mn spins, so the free energy gain from delocalizing the electrons would be greater within the planes, where a large number of spins can participate in the ferromagnetic cluster, than between the neighboring planes, where only two sites are involved. Nevertheless, the nearest-neighbor Mn-Mn distance between the planes is the same as within the plane, so it seems unlikely that the interplanar coupling would be more than an order of magnitude weaker than the intraplanar coupling, as required to explain the disparity in correlations.

The second interpretation is that there is a canting of the spins in neighboring planes, $i.e.$ the average value of θ is non-zero. Measurements of spinwave energies in $LaMnO_3$ [15,16] have provided evidence of competing ferro- and antiferromagnetic exchange interactions of the usual Heisenberg form in a related structure. However, nearest-neighbor Heisenberg exchange, whose energy is proportional to $S^2 cos\theta$, will only produce collinear ferro- or antiferromagnetic ordering, except when strong magnetocrystalline anisotropy tilts the spins away from

symmetry directions. In $La_{1.2}Sr_{1.8}Mn_2O_7$, there is no buckling of the MnO_2 planes to induce such tilts [4]. On the other hand, the energy of double exchange interactions for a pair of spins depends on $cos\theta/2$ [17] making non-collinear spin correlations, *i.e.* with a minimum free energy at $\theta \neq 0$ or π, in zero field a possibility when double exchange and superexchange are competing, as first pointed out by de Gennes [10]. The observed modulation gives an average cant angle of $(86.6 \pm 1.5)°$ at 125 K in zero field which suggests that the competing interactions are of the same order of magnitude in this compound.

We have repeated the scans with a magnetic field applied vertically *i.e.* parallel to [0k0]. As expected, the modulation becomes stronger with field [see Fig. 2(b)], corresponding to a reduction of the cant angle at 125 K to $(74.1 \pm 2.1)°$ at H = 1 T, although there is very little change at H = 0.5 T. Increasing the field still further to 2 T reduces the cant angle to $(53 \pm 6)°$, but results in a strong decrease of the scattering intensity because the spin fluctuations have been reduced by the growth of three-dimensional (3D) magnetic order.

When the temperature is reduced to T_C, the modulation increases so that the zero-field and 0.5 T data at 112 K are very similar to the 1 T and 2 T data, respectively, at 125 K. Since the correlations between different bilayers have also built up considerably at this temperature, with increases in scattering around the 3D Bragg points such as at (101), it appears that the additional interplanar exchange coupling favors a smaller cant angle. Below T_C, Argyriou *et al* [5] have shown that the ferromagnetic phase is probably also canted but the precise angle is not known.

We have also determined the temperature dependence of the in-plane correlation lengths. In order to optimize the energy integration of the scans, we have performed them with the scattered wavevector, k_f, parallel to the rods. Surprisingly, the correlation length does not appear to diverge at T_C only reaching a value of 12.1 $\mathring{A}$ (Fig. 3). Although this means that we are never in the critical regime, power-law scaling of the correlation length is consistent with our results, with an exponent ν that depends strongly on the assumed value of the 2D critical temperature, T_C^{2D}, *i.e.* the temperature at which 2D ordering would occur in the absence of 3D interactions. A mean field exponent of $\nu = 0.5$ gives $T_C^{2D} = 98.2$ K while, at the other extreme, the 2D-Ising exponent $\nu = 1$ gives $T_C^{2D} = 63.0$ K.

The lack of divergence of the 2D-correlation length at T_C may be evidence that the phase transition is actually weakly first-order. For example, either electron-lattice interactions may play a role in driving this transition, since lattice parameter anomalies are also observed in this temperature range [4], or the ordering may be unconventional, *e.g.* consider the small-to-large polaron transition proposed by Röder *et al* [8]. However, there are also signs of a build-up of 3D correlations from 120 to 112 K, so it

may be that there is a crossover to 3D critical scaling very close to T_C. Since recent spinwave measurements indicate that the exchange coupling within the bilayer is two orders of magnitude greater than between bilayers [18], such a 3D crossover would be expected to occur within only $\sim$1 K of T_C.

Below T_C, we observe scaling of the magnetic order parameter with no clear evidence that the transition is interrupted by a first-order transition [19]. Scans through the (002) Bragg peak, which has extremely weak nuclear intensity, show that the intensity, which is proportional to M^2, scales as $t^{2\beta}$ where $t = (T_C - T) / T_C$ from 100 to 111 K, with $T_C = (111.7 \pm 0.2)$ K and $\beta = 0.13 \pm 0.01$. The small value for β indicates that the fluctuations below T_C are still strongly two-dimensional (*e.g.* $\beta = 0.125$ in the 2D Ising model). Figure 4 shows that there is a strong fluctuation tail that extends to $\sim$3% above the scaling value of T_C. Superimposed on the neutron data in Fig. 4 are in-plane conductance results on a single crystal (grown in the same way as the neutron sample) which has $T_C = 113.3$ K and $\beta = 0.17 \pm 0.01$ determined between 90 and 110 K. When scaled to the slightly different T_C values, the coincidence of the two sets of data, even into the fluctuation regime above T_C, is manifest. This shows that in the critical regime, the electrical conductance has the same temperature dependence as the squared zero-field magnetization, a direct correlation which, to our knowledge, has not been predicted [20,21]. If this connection is universal, it will constrain theoretical approaches to the spontaneous magnetic state below T_C.

In conclusion, we have observed evidence that Mn spins in neighboring layers within each bilayer of the naturally-layered CMR manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ are strongly canted above T_C at an angle that is both temperature and field dependent. It is possible to identify this canting because of the reduced dimensionality of the magnetic correlations, so if it also occurs in the regular perovskites, it would be more difficult to observe. The growth of 3D correlations close to T_C produces a reduction in the average cant angle although the in-plane correlation length never fully diverges, possibly indicating that the transition is weakly first-order. The direct link between magnetic order and electronic transport is clearly seen in the 2D critical scaling just below T_C.

*Also at the University of Maryland, College Park, MD 20742

[1] Y. Moritomo *et al.*, Nature **380**, 141 (1996).

[2] T. Kimura *et al.*, Science **274**, 1698 (1996).

[3] T. G. Perring *et al.*, Phys. Rev. Lett. **78**, 3197 (1997).

[4] J. F. Mitchell *et al.*, Phys. Rev. B **55**, 63 (1997).

[5] D. N. Argyriou *et al.*, Phys. Rev. Lett. **78**, 1568 (1997).

[6] P. D. Battle *et al.*, J. Phys. Cond. Matt. **8**, L427 (1996).

[7] A. J. Millis, B. I. Shraiman, and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).

[8] H. Röder, J. Zang, and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).

[9] J. M. De Teresa *et al.*, Nature **386**, 256 (1997).

[10] P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

[11] S. K. Mishra *et al.*, Phys. Rev. B **55**, 2725 (1997).

[12] D. Golosov, M. R. Norman, and K. Levin, to be published (1997).

[13] R. Busch *et al*, Phys. Rev. Lett. **69**, 522 (1992).

[14] C.D. Potter *et al.*, Phys. Rev. B, in press, "Two-dimensional intrinsic and extrinsic ferromagnetic behavior of layered $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystals" (1997).

[15] K. Hirota *et al.*, J. Phys. Soc. Jpn. **65**, 3736 (1996).

[16] F. Moussa *et al.*, Phys. Rev. B **54**, 15149 (1996).

[17] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[18] S. Rosenkranz *et al.*, to be published.

[19] The absence of any hysteretic behavior also indicates that, if the transition is first-order, it is only weakly so.

[20] N. Furukawa, J. Phys. Soc. Jpn. **63**, 3214 (1994).

[21] T. Okabe, J. Phys. Soc. Jpn. **64**, 3442 (1995).

FIGURE CAPTIONS

FIG. 1. Diffuse neutron scattering above T_C (at 130 K) in the $(0k0)$ plane showing the rod of magnetic scattering along the $[h0l]$ direction.

FIG. 2. (a) Diffuse neutron scattering at 125 K along the $\mathbf{Q} = [h\ 0\ 1.833]$ direction. The solid line is a fit to a Lorentzian lineshape convolved with the instrumental resolution. The half-width, $\kappa = 0.102\ \mathring{A}^{-1}$, is the inverse correlation length within the two-dimensional planes. (b) Diffuse scattering at 125 K along the $\mathbf{Q} = [0.95\ 0\ l]$ direction with an applied field of 0 T (filled circles), 1T (open circles) and 2 T (filled squares). The solid lines are fits to Eq. 2 with $\theta = 86.6°$, $74.1°$ and $53°$, respectively.

FIG. 3. In-plane correlation length *vs* temperature. The solid line is a power-law fit to the data with $T_C^{2D} = (75 \pm 11)$ K and exponent $\nu = 0.84 \pm 0.15$. The dashed and chain lines show fits using the 2D Ising and mean field values of $\nu = 1$ and 0.5, respectively. The inset shows the inverse correlation length similarly fitted. The arrows show the value of $T_C = 111.7$ K determined from scaling below the transition.

FIG. 4. Intensity of (002) Bragg peak *vs* reduced temperature $(T_C - T)/T_C$. The dashed line is a power-law fit from 100 K to 111 K with $T_C = (111.7 \pm 0.2)$ K and $\beta = 0.13 \pm 0.01$. The solid line is the in-plane electrical conductance measured on a sample of the same composition with $T_C = 113.3$ K. The inset shows the same measurements over an expanded temperature range.
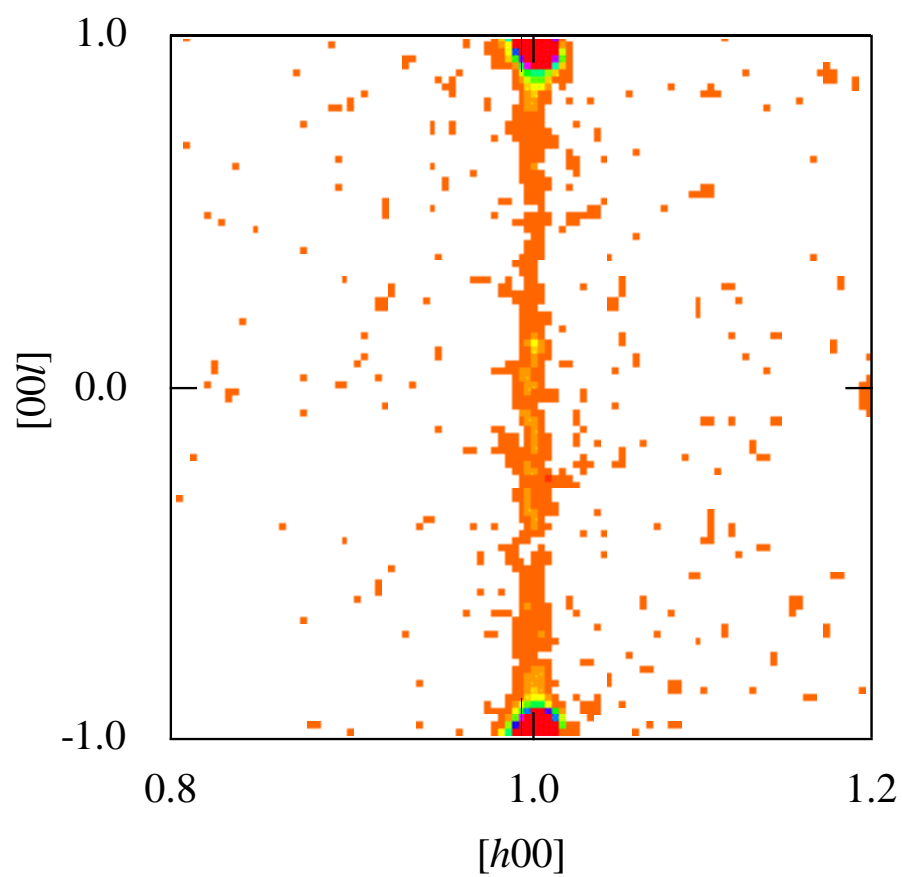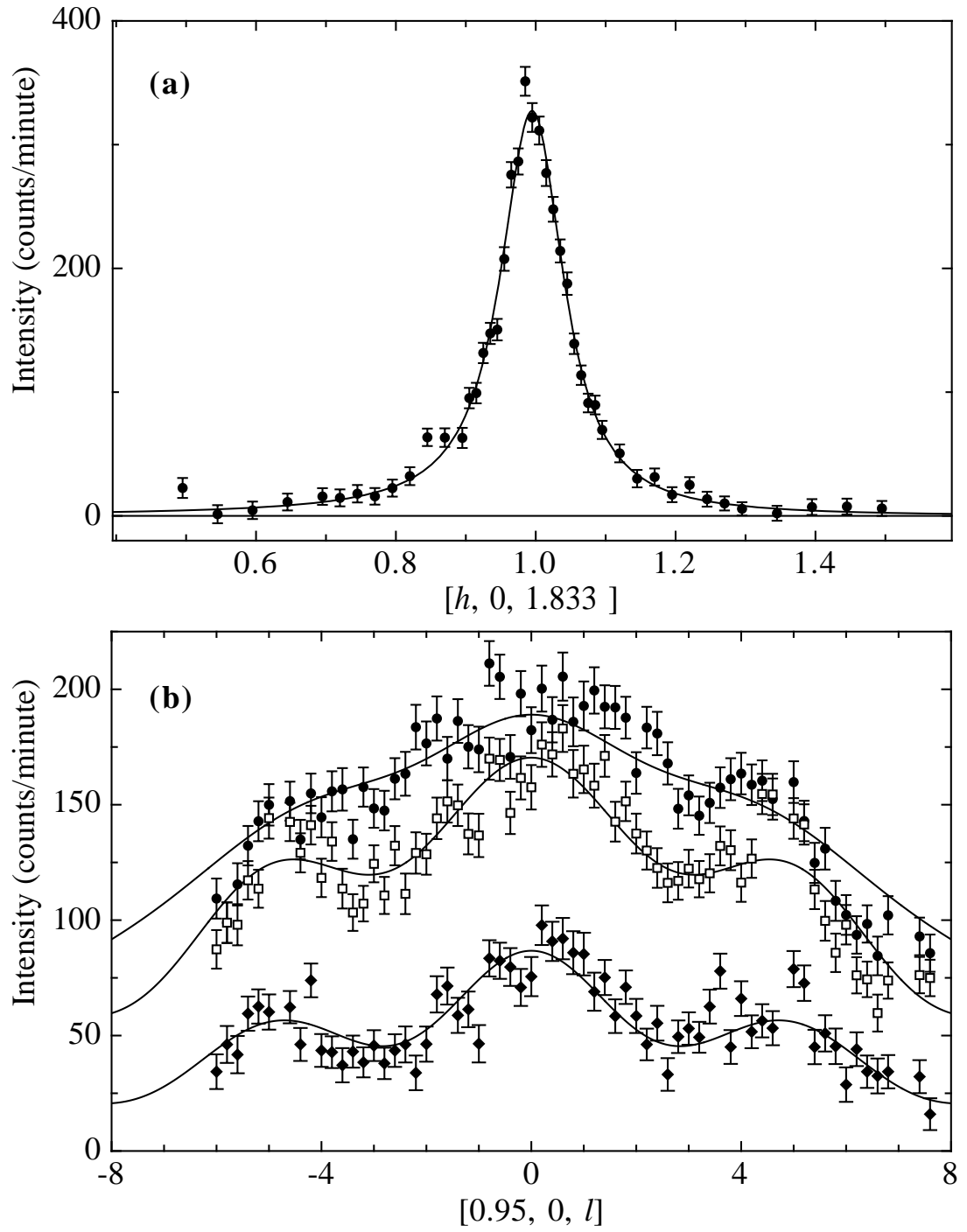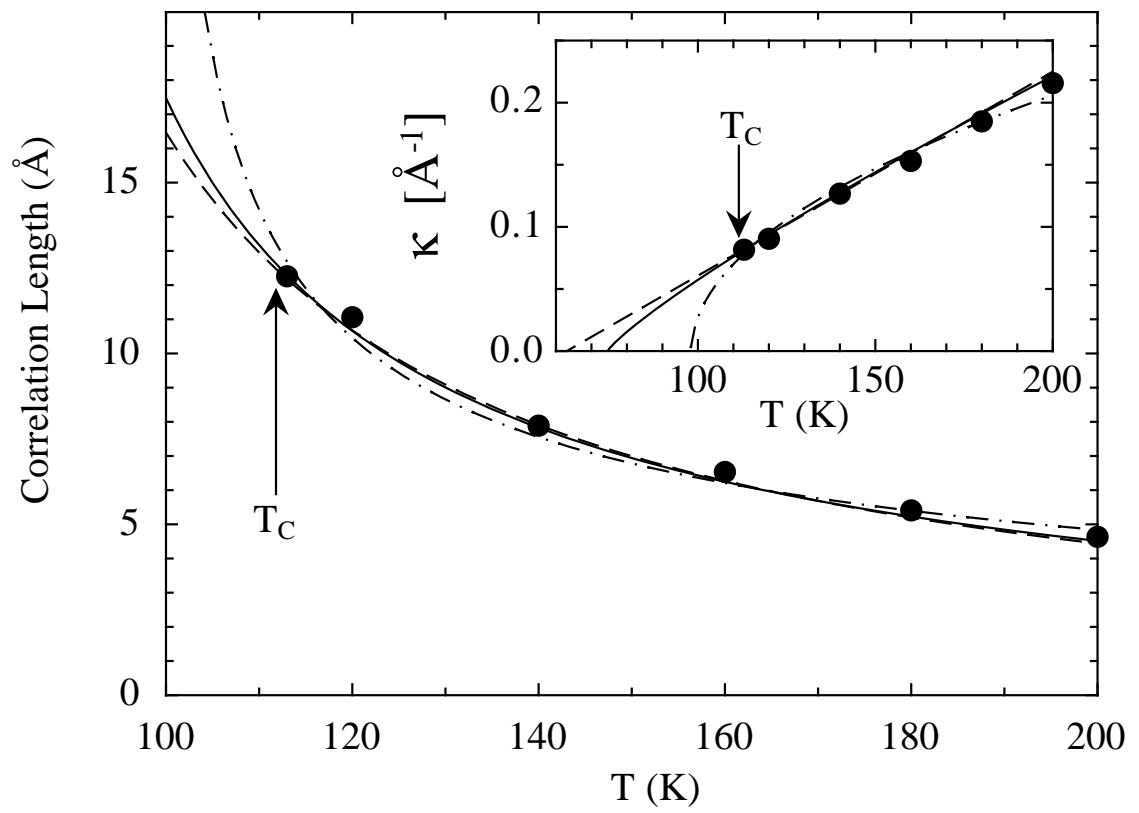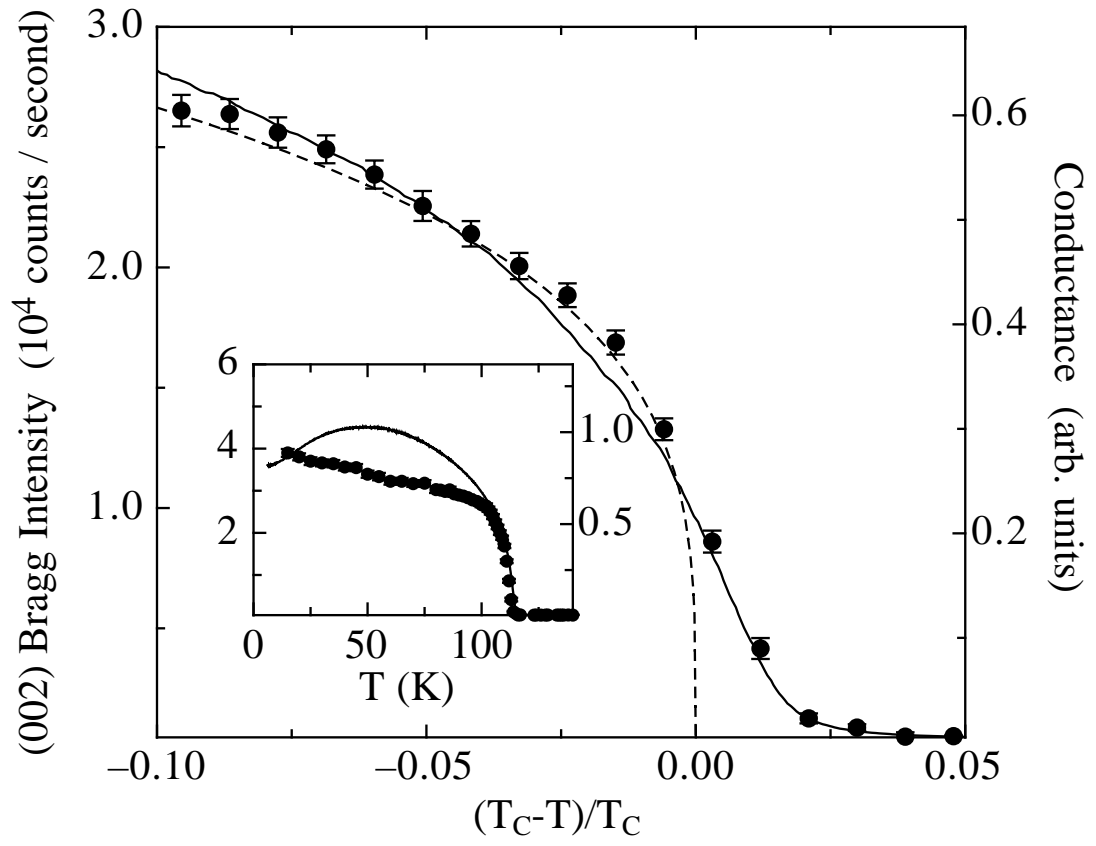
FIG. 1

(a)

(b)

FIG. 2

6

FIG. 3

FIG. 4